2,3,6,7-Tetramethoxy-9,10-anthraquinone

Akira Ohta,[a] Kazuki Hattori,[a] Takeshi Kawase,[b] Takashi Kobayashi,[c] Hiroyoshi Naito[c] and Chitoshi Kitamura[b]*

[a]Department of Chemistry, Faculty of Science, Shinshu University, 3-1-1 Asahi, Matsumoto, Nagano 390-8621, Japan, [b]Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2280, Japan, and [c]Department of Physics and Electronics, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuencho, Naka-ku, Sakai, Osaka 599-8531, Japan

Correspondence e-mail: kitamura@eng.u-hyogo.ac.jp

Molecules of the title compound, $C_{18}H_{16}O_6$, are almost planar [maximum deviation = 0.096 (4) Å] and reside on crystallographic centres of inversion. They adopt a conformation in which the C_{methyl}—O bonds are directed along the molecular short axis [C—C—O—C torsion angles of −175.3 (3) and 178.2 (3)°]. In the crystal, molecules adopt a slipped-parallel arrangement with π–π stacking interactions along the a axis with an interplanar distance of 3.392 (4) Å. Weak C—H···O interactions link the molecules into sheets parallel to $(10\bar{2})$.

Related literature

For a study of the effects of alkoxy substituents on the structures and solid-state photophysics, see: Ohta *et al.* (2012). For the synthesis, see: Boldt (1967). For a related structure, see: Kitamura *et al.* (2009).
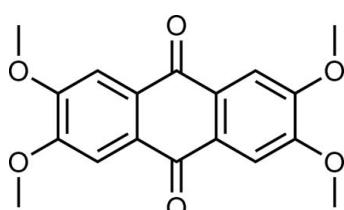
Experimental

Crystal data

$C_{18}H_{16}O_6$	$M_r = 328.31$

Triclinic, $P\bar{1}$
$a = 4.6607$ (4) Å
$b = 8.4769$ (9) Å
$c = 9.8110$ (9) Å
$\alpha = 94.859$ (3)°
$\beta = 91.410$ (2)°
$\gamma = 97.278$ (2)°

$V = 382.87$ (6) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 223$ K
$0.50 \times 0.06 \times 0.05$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer
3738 measured reflections

1725 independent reflections
977 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.234$
$S = 1.16$
1725 reflections

111 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8A···O1[i]	0.97	2.58	3.391 (5)	142
C9—H9B···O2[ii]	0.97	2.54	3.494 (4)	168

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x + 2, -y + 1, -z + 1$.

Data collection: *RAPID-AUTO* (Rigaku, 1999); cell refinement: *PROCESS-AUTO* (Rigaku, 1998); data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GG2091).

References

Boldt, P. (1967). *Chem. Ber.* **100**, 1270–1280.
Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Kitamura, C., Akamatsu, N., Yoneda, A. & Kawase, T. (2009). *Acta Cryst.* E**65**, o324.
Ohta, A., Hattori, K., Kusumoto, Y., Kawase, T., Kobayashi, T., Naito, H. & Kitamura, C. (2012). *Chem. Lett.* **41**, 674–676.
Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku (1999). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

2,3,6,7-Tetramethoxy-9,10-anthraquinone

Akira Ohta, Kazuki Hattori, Takeshi Kawase, Takashi Kobayashi, Hiroyoshi Naito and Chitoshi Kitamura

S1. Comment

9,10-Anthraquinone is an important molecule in the field of industrial dyes. We have recently been interested in the tuning of the solid-state optical properties by the introduction of substituents. As part of our program aimed at the elucidation of the effects of alkoxy substituents on the optical properties in the solid state (Ohta, *et al.*, 2012), we are in need of the information on the crystal structures of a variety of 2,3,6,7-tetraalkoxy-9,10-anthraquinones in order to clarify the correlation between crystal structures and the solid-state photophysics. Although the title compound is already known (Boldt, 1967), the X-ray structure was not reported to date. We report herein the crystal structure of the title compound (I).

The molecular structure of the title compound (I) is shown in Fig. 1. The molecule possesses a center of inversion, and half of the formula unit is crystallographically independent. The molecule is almost planar with the maximum deviation of 0.096 (4) Å for C8. The displacements of atoms O1, O2, O3, C8 and C9 relative to the plane of the anthraquinone framework are 0.023 (2), -0.002 (2), 0.013 (2), 0.096 (4), and 0.060 (3), respectively. The molecule prefers the conformation in which the C_{methyl}—O bonds are directed along the molecular short axis. The torsion angles of C3—C2—O2—C8 and C2—C3—O3—C9 are -175.3 (3) and 178.2 (3)°, respectively. This conformation is similar to the corresponding moiety in 2,3-dimethoxy-5,12-tetracenequinone (Kitamura, *et al.*, 2009). The molecules adopt a slipped-parallel arrangement as shown in Fig. 2. Then molecules are π-stacked along the *a* axis with an interplanar distance 3.392 (4) Å.

To examine the influence of crystal packing on the solid-state fluorescences, the fluorescence spectrum and the absolute quantum yield of (I) were measured with a Hamamatsu Photonics PMA11 calibrated optical multichannel analyzer with a solid-state blue laser (λ_{ex} = 377 nm) and a Labsphere IS IS-040-SF integrating sphere, respectively. The crystals showed negligible fluorescence (Φ = 0.002). The fluorescence quenching would be due to the π-stacked structure.

S2. Experimental

The title compound was prepared according to the literature procedure (Boldt, 1967). Single crystals suitable for X-ray analysis were obtained by recrystallization from DMF.

S3. Refinement

All the H atoms were positioned geometrically and refined using a riding model with C—H = 0.94 Å and U_{iso}(H) = $1.2U_{eq}$(C) for aromatic C—H, and C—H = 0.97 Å and U_{iso}(H) = $1.5U_{eq}$(C) for CH₃. The positions of methyl H atoms were optimized rotationally.
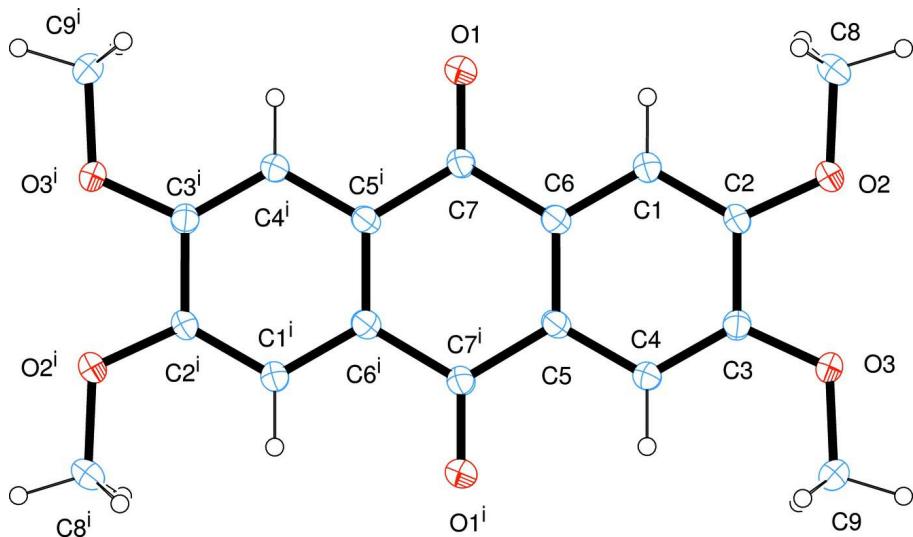
Figure 1

The molecular structure of the title compound (I), showing the atomic numbering numbering and 30% probability displacement ellipsoids. Symmetry code: (i) -*x*, -*y* + 1, -*z*.
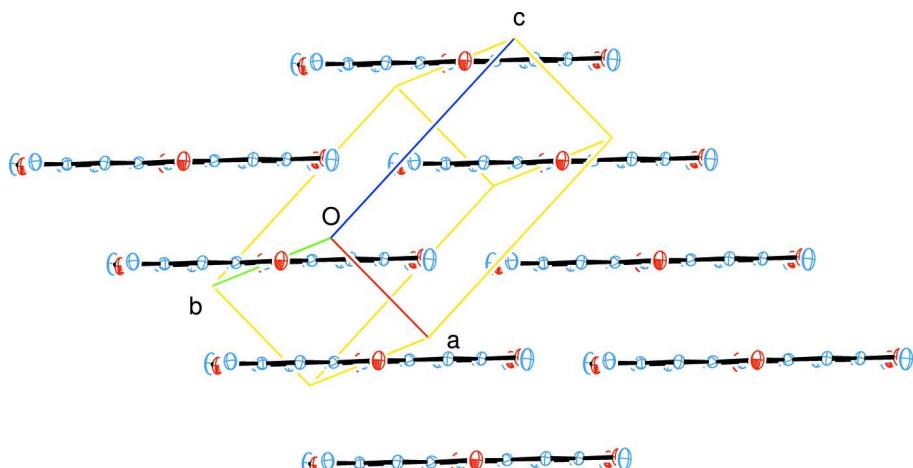
Figure 2

The packing diagram of (I). Hydrogen atoms are omitted for clarity.

2,3,6,7-Tetramethoxy-9,10-anthraquinone

Crystal data

$C_{18}H_{16}O_6$	$Z = 1$
$M_r = 328.31$	$F(000) = 172$
Triclinic, $P\overline{1}$	$D_x = 1.424$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 4.6607$ (4) Å	Cell parameters from 1977 reflections
$b = 8.4769$ (9) Å	$\theta = 3.1–27.5°$
$c = 9.8110$ (9) Å	$\mu = 0.11$ mm^{-1}
$\alpha = 94.859$ (3)°	$T = 223$ K
$\beta = 91.410$ (2)°	Needle, yellow
$\gamma = 97.278$ (2)°	$0.50 \times 0.06 \times 0.05$ mm
$V = 382.87$ (6) Å^3	

Data collection

Rigaku R-AXIS RAPID diffractometer	1725 independent reflections
Radiation source: fine-focus sealed x-ray tube	977 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.027$
Detector resolution: 10 pixels mm⁻¹	$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
ω scans	$h = -6 \rightarrow 5$
3738 measured reflections	$k = -10 \rightarrow 10$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.054$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.234$	
$S = 1.16$	H-atom parameters constrained
1725 reflections	$w = 1/[\sigma^2(F_o^2) + (0.1038P)^2 + 0.301P]$
111 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.39$ e Å⁻³
	$\Delta\rho_{min} = -0.44$ e Å⁻³

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.3162 (6)	0.2759 (3)	0.1180 (3)	0.0304 (7)
H1	0.2882	0.1685	0.082	0.036*
C2	0.5104 (6)	0.3236 (3)	0.2269 (3)	0.0282 (7)
C3	0.5524 (6)	0.4852 (3)	0.2811 (3)	0.0279 (6)
C4	0.3981 (6)	0.5939 (3)	0.2252 (3)	0.0293 (7)
H4	0.425	0.7012	0.2616	0.035*
C5	0.2021 (6)	0.5460 (3)	0.1150 (3)	0.0264 (6)
C6	0.1606 (6)	0.3872 (3)	0.0611 (3)	0.0274 (6)
C7	−0.0418 (6)	0.3343 (3)	−0.0564 (3)	0.0286 (6)
O1	−0.0753 (5)	0.1938 (3)	−0.1056 (2)	0.0421 (6)
C8	0.6538 (9)	0.0647 (4)	0.2327 (4)	0.0529 (10)
H8A	0.4579	0.0121	0.2389	0.079*
H8B	0.7865	0.0095	0.2828	0.079*
H8C	0.7052	0.0628	0.1374	0.079*
O2	0.6714 (5)	0.2264 (2)	0.2899 (2)	0.0369 (6)
C9	0.8062 (7)	0.6813 (4)	0.4442 (3)	0.0382 (8)
H9A	0.8839	0.7476	0.3745	0.057*

H9B	0.946	0.6892	0.5202	0.057*
H9C	0.6283	0.7173	0.4764	0.057*
O3	0.7479 (5)	0.5185 (2)	0.3876 (2)	0.0345 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0295 (15)	0.0273 (15)	0.0345 (15)	0.0050 (11)	−0.0052 (12)	0.0030 (12)
C2	0.0270 (14)	0.0262 (14)	0.0325 (14)	0.0079 (11)	−0.0031 (12)	0.0033 (11)
C3	0.0277 (14)	0.0278 (15)	0.0280 (14)	0.0026 (11)	−0.0024 (11)	0.0040 (11)
C4	0.0292 (14)	0.0235 (14)	0.0348 (15)	0.0034 (11)	−0.0048 (12)	0.0022 (11)
C5	0.0254 (14)	0.0226 (14)	0.0320 (14)	0.0048 (11)	0.0015 (12)	0.0039 (11)
C6	0.0274 (14)	0.0254 (15)	0.0299 (14)	0.0045 (11)	0.0015 (12)	0.0037 (11)
C7	0.0262 (14)	0.0255 (14)	0.0342 (15)	0.0040 (11)	−0.0034 (12)	0.0030 (11)
O1	0.0474 (14)	0.0269 (12)	0.0514 (14)	0.0090 (9)	−0.0156 (11)	−0.0022 (9)
C8	0.062 (2)	0.0276 (17)	0.070 (2)	0.0148 (15)	−0.025 (2)	−0.0001 (16)
O2	0.0405 (12)	0.0287 (12)	0.0423 (12)	0.0116 (9)	−0.0126 (10)	0.0013 (9)
C9	0.0418 (18)	0.0317 (17)	0.0392 (16)	0.0025 (13)	−0.0133 (14)	−0.0007 (13)
O3	0.0377 (12)	0.0289 (11)	0.0356 (11)	0.0049 (8)	−0.0145 (9)	−0.0002 (8)

Geometric parameters (Å, º)

C1—C2	1.382 (4)	C6—C7	1.474 (4)
C1—C6	1.404 (4)	C7—O1	1.236 (3)
C1—H1	0.94	C7—C5[i]	1.479 (4)
C2—O2	1.359 (3)	C8—O2	1.428 (4)
C2—C3	1.414 (4)	C8—H8A	0.97
C3—O3	1.356 (3)	C8—H8B	0.97
C3—C4	1.379 (4)	C8—H8C	0.97
C4—C5	1.397 (4)	C9—O3	1.434 (3)
C4—H4	0.94	C9—H9A	0.97
C5—C6	1.392 (4)	C9—H9B	0.97
C5—C7[i]	1.479 (4)	C9—H9C	0.97
C2—C1—C6	120.2 (3)	O1—C7—C6	121.0 (2)
C2—C1—H1	119.9	O1—C7—C5[i]	120.7 (2)
C6—C1—H1	119.9	C6—C7—C5[i]	118.3 (2)
O2—C2—C1	125.2 (3)	O2—C8—H8A	109.5
O2—C2—C3	114.9 (2)	O2—C8—H8B	109.5
C1—C2—C3	119.9 (2)	H8A—C8—H8B	109.5
O3—C3—C4	125.5 (3)	O2—C8—H8C	109.5
O3—C3—C2	114.8 (2)	H8A—C8—H8C	109.5
C4—C3—C2	119.7 (2)	H8B—C8—H8C	109.5
C3—C4—C5	120.5 (3)	C2—O2—C8	117.2 (2)
C3—C4—H4	119.7	O3—C9—H9A	109.5
C5—C4—H4	119.7	O3—C9—H9B	109.5
C6—C5—C4	119.9 (3)	H9A—C9—H9B	109.5
C6—C5—C7[i]	120.8 (2)	O3—C9—H9C	109.5

C4—C5—C7ⁱ	119.3 (2)	H9A—C9—H9C	109.5
C5—C6—C1	119.7 (3)	H9B—C9—H9C	109.5
C5—C6—C7	120.9 (2)	C3—O3—C9	117.4 (2)
C1—C6—C7	119.3 (3)		
C6—C1—C2—O2	179.8 (3)	C4—C5—C6—C7	−179.1 (3)
C6—C1—C2—C3	0.0 (4)	C7ⁱ—C5—C6—C7	0.6 (5)
O2—C2—C3—O3	0.2 (4)	C2—C1—C6—C5	−0.1 (4)
C1—C2—C3—O3	−180.0 (3)	C2—C1—C6—C7	179.0 (3)
O2—C2—C3—C4	−179.5 (3)	C5—C6—C7—O1	178.8 (3)
C1—C2—C3—C4	0.3 (4)	C1—C6—C7—O1	−0.3 (4)
O3—C3—C4—C5	179.9 (3)	C5—C6—C7—C5ⁱ	−0.6 (5)
C2—C3—C4—C5	−0.4 (4)	C1—C6—C7—C5ⁱ	−179.7 (3)
C3—C4—C5—C6	0.3 (4)	C1—C2—O2—C8	4.9 (5)
C3—C4—C5—C7ⁱ	−179.4 (3)	C3—C2—O2—C8	−175.3 (3)
C4—C5—C6—C1	0.0 (4)	C4—C3—O3—C9	−2.1 (4)
C7ⁱ—C5—C6—C1	179.7 (3)	C2—C3—O3—C9	178.2 (3)

Symmetry code: (i) −x, −y+1, −z.

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C8—H8A⋯O1ⁱⁱ	0.97	2.58	3.391 (5)	142
C9—H9B⋯O2ⁱⁱⁱ	0.97	2.54	3.494 (4)	168

Symmetry codes: (ii) −x, −y, −z; (iii) −x+2, −y+1, −z+1.